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Electrochemical oxygen reduction to hydrogen peroxide via a two-electron transfer pathway on carbon-based single-atom catalysts

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Electrochemical reduction of oxygen is considered as a new strategy to achieve decentralized preparation of hydrogen peroxide (H_2O_2) in a green manner. As a promising new type of catalytic material, carbon-based single-atom catalysts can achieve wide-range adjustments of the electronic structure of the active metal centers while also maximize the utilization of metal atoms, towards electrochemical production of H_2O_2 from the selective two-electron transfer oxygen reduction reaction (ORR). Herein, starting from the reviewing of characterizing methods and reaction mechanisms of ORR via two-electron and four-electron transfer pathways, the vital role of binding strength between OOH intermediate and active sites in determining the activity and selectivity towards H_2O_2 production is revealed and illustrated. Currently reported carbon-based single-atom catalysts for H_2O_2 production have been systematically summarized and critically reviewed. Moreover, with the underpinning chemistry to improve the overall efficiency, three aspects concerning the central metal atoms,

coordinated atoms and environmental atoms were comprehensively analyzed. Based on the understanding of the most current progresses, some predictions for future H_2O_2 production via electrochemical routes are offered, which include catalyst designs at atomic levels, new synthesis strategies and characterization techniques, as well as interfacial superwetting interaction engineering at electrode and device levels.

1. Introduction

Hydrogen peroxide, as one of the 100 most important chemical compounds in the world,^[1] is widely used as an environmentally friendly oxidant in industry and households, including pulp and textile bleaching,^[2] wastewater treatment,^[3] chemical synthesis,^[4–6] energy carrier,^[7–9] first-aid kits for sterilization, and semi-conductor cleaning. Currently, nearly 95% of hydrogen peroxide is produced by the anthraquinone process,^[10] which relies on the sequential hydrogenation and oxidation of an anthraquinone molecule over Ni or supported Pd catalysts in an organic solvent.^[11] In addition to environmental issues, the large-scale production equipment and the subsequent addition and removal of stabilizers during transportation have greatly increased the cost of this production system. One alternative route is the direct synthesis using H_2 and O_2 .^[12–14] However, the low H_2O_2 selectivity and the safety issues of mixing hydrogen and oxygen in the production process hinder its practical application.^[15] Therefore, establishing a small-scale, safe, direct, efficient, and environmentally friendly decentralized production process of H_2O_2 is a shared goal of both industry and academia.

The development of electrochemistry provides new opportunities for the synthesis of H_2O_2 , which can be produced while avoiding the aforementioned issues^[16] through the deliberate control of the oxygen reduction reaction (ORR) via the two-electron transfer pathway. Moreover, the continuous H_2O_2 production strategy through the two-electron ORR can also be coupled with new energy devices such as fuel cells, further illustrating its advantages of killing two birds with one stone.^[15] In the 1930s, Berl firstly reported the electrochemical H_2O_2

production by two-electron ORR, which was then developed by the Dow and Huron Technologies, Inc. and experienced a long history of development, finally commercialized in 1991^[17] (Huron-Dow process). Recently, the excellent performance in water and wastewater treatment of the Electro-Fenton process,^[18,19] which was developed by the Huron-Dow process, has further expanded the application scenarios of H₂O₂. Meanwhile, the academic community has made the synthesis of H₂O₂ via two-electron ORR more valued.^[20] Although remarkable progress has been made, the design of efficient catalysts and electrodes for H₂O₂ synthesis is still a challenge for the further developing the H₂O₂ industry.

Throughout the development history of two-electron ORR catalysts, precious metal alloy nanocrystals^[16,21–23] and metal-free carbon-based materials^[24–27] alternately played vital roles. Although some promising results have been achieved in recent decades, there are still some inherent problems in those materials. Among them, reserves and cost issues hinder the widespread use of precious metal catalysts, despite their excellent activity and selectivity. Metal-free heteroatoms-doped carbon materials were first studied as alternatives to replace precious metal catalysts for the four-electron ORR in fuel cells due to their abundant reserves and superb activities^[28–33] However, research subsequently proved that the high overpotential of the carbon-based materials toward ORR was due to its relatively high selectivity to H₂O₂,^[34,35] which led to growing attention focusing on their selective production of H₂O₂. However, high ORR overpotential of carbon-based material in the acid medium still matters despite H₂O₂ superior selectivity.^[36]

With the advancement of synthesis and characterization technologies, the design of active sites and verification of catalysis hypotheses at the atomic scale becomes a reality, which further inducts the catalysis community into the era of single-atom catalysts (SACs).^[37,38] SACs followed and fully realized the instruction of increasing the amount of active sites by

minimizing the geometric size.^[39,40] In addition to the maximum atom utilization, the introduction of transition metals into carbon-based frameworks, creating active moieties with stabilized and activated metal cations, is a broadly reported strategy which could combine SACs with excellent conductivity, a large surface area and a high pore volume for mass transportation of carbon materials.^[41] Furthermore, in addition to the wide range of transition metal candidates, intrinsic chemical properties which are critical for the catalytic activity of metal active center, such as electron density,^[42,43] ligand effect and geometric structure^[44] will affect adsorption behavior and can be adjusted through the modulation of coordination atoms or environmental atoms. The above merits may make carbon-based SACs a candidate with excellent prospects in both catalytic activity and selectivity towards two-electron ORR.

In this review, begin with the proposed ORR pathways for both four-electron and two-electron transfer conversion, the role of binding strength between intermediate OOH and active sites in influencing the H₂O₂ activity and selectivity is illustrated. Moreover, the current progresses of carbon-based SACs in modulating activity and selectivity towards two-electron transfer ORR are systematically summarized. Three aspects are studied regarding the regulation of the central metal atoms, the coordinated atoms, and the environmental atoms, respectively. Theoretical explanations as well as experimental results are equally underlined to unfold the structure-performance relationship between the configuration of the carbon-based SACs active sites and the intrinsic two-electron transfer ORR electrocatalytic activity and selectivity. Finally, design principles and predictions of carbon-based SACs for further development of two-electron transfer ORR are proposed.

2. Performance Characterization: Rotating-Ring Disk Electrode

The electrochemical performance of two-electron transfer ORR is usually investigated by the rotating ring-disk electrode (RRDE) technique.^[11,45,46] RRDE working with a three electrodes

cell using liquid electrolytes is a simple, yet powerful, electrochemical method to quantitatively measure the production of H_2O_2 by ORR. Compared with larger-scale tests in real devices, RRDE does not rely on the membrane electrode assembly (MEA) system with solid electrolytes but uses liquid electrolytes, which is simpler for further optimization and repeatable stability on a laboratory scale. This feature makes RRDE an irreplaceable method in intrinsic ORR performance characterization.

Scheme 1. Schematic of RRDE set-up and basic operating principles. O_2 reduction occurs at the catalyst deposited disk electrode producing both H_2O_2 and H_2O . The H_2O_2 is radially transferred to the Pt ring electrode due to concentric rotations, where it is oxidized back to O_2 .

Generally, a single compartment (Scheme 1) is where all the electrochemical experiments are performed, and N_2 or O_2 -saturated aqueous solution with different pH values are used as electrolytes. Typically, a glassy carbon disk with Pt ring electrode is employed as the working electrode. The catalyst can be either a bulk, extended planar surface, or a thin film of supported nanoparticles.^[45,46] H_2O_2 produced at the disk electrode is radially transferred to the concentric Pt ring electrode by the forced convection caused by the rotating motion of the electrode.^[47] The measured potentials are quoted with respect to the reversible hydrogen electrode (RHE) and are corrected for ohmic losses and background current. To quantify the amount of

generated H_2O_2 , the ring is set at $\approx 1.2 \text{ V}_{\text{RHE}}$, at which potential the ORR current is negligible and the H_2O_2 oxidation back to O_2 at the ring electrode is mass transport limited.

The selectivity for H_2O_2 production can be calculated in two ways from measured currents of O_2 reduction at the disk and H_2O_2 oxidation at the Pt ring.

(1) The Faradaic efficiency (FE), considering that the disk current (I_D) is the total current of the reduction of oxygen to water ($I_{\text{H}_2\text{O}}$) and H_2O_2 ($I_{\text{H}_2\text{O}_2}$), ($I_D = I_{\text{H}_2\text{O}} + I_{\text{H}_2\text{O}_2}$). By using the ring currents (I_R) and the collection efficiency N of the ring currents: $I_{\text{H}_2\text{O}_2} = I_R N^{-1}$, the selectivity can be expressed by Faradaic efficiency (%):

$$\lambda_{\text{Faradaic}} = \frac{I_R N^{-1}}{I_D} \times 100 \quad (1)$$

(2) In terms of the fraction of O_2 used for H_2O_2 , the selectivity for H_2O_2 formation (O_2 efficiency) could be calculated from the ratio between O_2 consumption rate toward H_2O_2 ($n_{\text{O}_2(2e^-)} = \frac{I_{\text{H}_2\text{O}_2}}{2F}$) and total consumption rate ($n_{\text{O}_2} = \frac{I_{\text{H}_2\text{O}_2}}{2F} + \frac{I_{\text{H}_2\text{O}}}{4F}$),^[45] the selectivity can be expressed by O_2 efficiency (%):

$$\lambda_{\text{O}_2} = \frac{2I_R N^{-1}}{I_D + I_R N^{-1}} \times 100 \quad (2)$$

Where the collection efficiency (N) can be determined from the measurement of hexacyanoferrate (III) reduction for every RRDE system, and F is Faraday constant.

Figure 1. Typical RDE voltammograms at different rotation speeds (400 rpm-2025 rpm) and (b) the corresponding Koutecky-Levich plots of Fe-NSC.^[42], Copyright © 2020, Springer Nature.

To understand detailed information about the relationship between kinetic activity and mass transport of reactants, a Koutecky-Levich (K-L) plot obtained from polarization curves at a series of increasing rotation speeds (Figure 1a) could be useful. The transferred electron number (n) and kinetic current density (j_k) can be calculated from the Koutecky-Levich equation by measured parameters (Figure 1b). In the K-L equation (Equation (3)), j is the measured current density, which is related to the kinetic current density (j_k) of disk current and the diffusion-limited current (j_d) of disk current, and ω is the angular velocity of the rotating disk electrode.

$$\frac{1}{j} = \frac{1}{j_d} + \frac{1}{j_k} = \frac{1}{j_k} + \frac{1}{B\sqrt{\omega}} \quad (3)$$

$$B = 0.62 \cdot n \cdot F \cdot D_{O_2}^{\frac{2}{3}} \cdot \nu^{-\frac{1}{6}} \cdot C_{O_2} \quad (4)$$

$$j_k = nFKC_{O_2} \quad (5)$$

in which the B factor and j_k are given by Equations (4) and (5), where n is the number of transferred electrons, D_{O_2} and C_{O_2} are the diffusivity and solubility of oxygen, respectively, ν is the kinematic viscosity of the electrolyte, and K is the electron transfer rate constant.

In addition to electrochemical methods, the concentration of H_2O_2 produced in the electrolyte can also be measured by a traditional titration method. Cerium sulfate, $\text{Ce}(\text{SO}_4)_2$, is used as a titration indicator based on the reaction of Ce^{4+} with H_2O_2 :

in which the yellow Ce^{4+} will become colourless Ce^{3+} according to the stoichiometric ratio, and this colour change can be quantitatively measured by ultraviolet-visible spectroscopy, with the UV wavelength around 316 nm.^[26] H_2O_2 will undergo a catalytic but non-electrochemical self-disproportionation reaction over the surface of the applied catalyst, which represents a serious problem in the synthesis of H_2O_2 via the two-electron ORR. In order to obtain intrinsic production of H_2O_2 , the amount of chemical disproportionation of H_2O_2 could be identified by dispersing catalysts in H_2O_2 solution at the same temperature and measuring the H_2O_2 concentration by titration method as mentioned above at specified time intervals. The electrochemical H_2O_2 reduction experiment is basically the same as that for ORR except for the electrolyte being saturated with N_2 instead of O_2 and containing $10 \times 10^{-3} \text{M}$ H_2O_2 .^[48]

3. Rational design of single-atom catalysts.

SACs have shown excellent catalytic performances in ORR, but reports have mostly focused on the four-electron transfer ORR used in fuel cell systems,^[49–52] while the two-electron transfer ORR used for the synthesis of H_2O_2 has rarely been reported. This is mainly due to the different reaction paths of these two reactions. In addition to the requirement for the reactivity, the selectivity of the target product is also an important indicator for evaluating the performance of SACs,^[53–55] which required the fine modulation of catalyst. A deep understanding of the differences in reaction paths will help us to better balance the activity and selectivity, and thus benefit the design of the catalyst.

The electrochemical reversible redox reaction of oxygen to water, including four-electron transfer ORR and its reverse reaction, i.e., water oxidation, can be summarized by Equation 7:^[56,57]

In general, there are three widely accepted mechanisms for ORR:

1. The dissociation mechanism, where the O-O bond is directly broken to form two adsorbed $*O$ as the adsorption occurs, followed by a proton-coupled electron transfer (PCET) step to form $*OH$, successively to $*H_2O$. However, due to no contiguous active sites available on SACs surfaces, the O-O bond cleavage is not possible, which excludes the possibility of the dissociative mechanism.^[58]

Scheme 2. Unified two (red part)- and four (blue and green part)-electron pathways in electrochemical ORR, and the H₂O₂ disproportionation pathway (purple part).

2. The association mechanism, where O₂ first adsorbs onto the active site (*) and undergoes a PCET step to form $*OOH$, as shown in Equation 8, then, a cleavage of O-O bond occurs to form $*O$ (Equation 9,10), successively to H₂O to fulfil a four-electron ORR (blue part in Scheme 2).

3. The peroxide mechanism, after O_2 being adsorbed at the active site, it undergoes two PCET steps in succession to generate $*HOOH$ (red part in Scheme2, Equation 8 and 11, overall Equation 12), where the O-O bond being broken to form $*OH$ following generation of H_2O (green part in Scheme 2).

As mentioned above, the non-electrochemical disproportionation of H_2O_2 usually happens as shown in Equation 13 and purple part in Scheme 2.

Therefore, as an intermediate product, the selective synthesis of H_2O_2 significantly affected by breaking of the O-O bond, which will induce the undesired formation of H_2O . From this perspective, it is critical to intentionally protect the O-O bond from cleavage to improve the intrinsic selectivity towards H_2O_2 . Simultaneously, the extended residence time of $*OOH$ on active sites is not conducive to the formation of peroxide, which will cause succeeding $*OOH$ dissociation (the breaking of O-O bond). Therefore, other factors such as enhancing product mass transfer efficiency, reducing the density of active sites, and adjusting the pH of the electrolyte can also repel H_2O_2 product and thereby improve the overall selectivity of the reaction.^[11,59,60]

As the only intermediate species of the two-electron transfer ORR, the adsorption behaviour of OOH on active sites directly determines the final reaction path, more precisely, its proper bonding with the active site can effectively preserve O-O bond.^[21] Ideally, the active site should possess strong adsorption for O₂ molecules to trigger the reaction and then to induce the formation of *OOH, while at the same time exhibiting weak adsorption for OOH to smooth the way for its desorption from the surface to produce H₂O₂. Theoretically, an optimized active site for H₂O₂ synthesis should minimize the kinetic barriers for Equations 8 and 11 to provide high activity. Meanwhile, the catalyst needs to maximize the barrier for *OOH dissociation or reduction to *O and *OH (Equations 9 and 10) to achieve high selectivity. As an inherent nature of SACs, the atomically dispersed active sites prevent O-O bond from splitting, which improves the H₂O₂ selectivity of SACs and makes it an advantaged catalyst to a certain extent.^[61,62]

Figure 2. (a) and (b) Sabatier volcanic plots summary of some reported samples. The limiting potential is plotted as a function of ΔG_{OOH} . The blue line represents two-electron reduction, and the black line represents

four-electron reduction. The model used here is based on (c), where in (a) all the coordinated atoms are N and no environmental atoms, in (b) all the coordinated atoms are N, other modifies will be discussed in detail later. The data from (a) Ref^[11], Copyright 2018, American Chemical Society and Ref^[16], Copyright 2013, Nature Publishing Group. (b) data from Ref^[63], Copyright 2020, Nature Publishing Group and Ref^[16], Copyright 2013, Nature Publishing Group. (c) Geometric structure scheme of carbon-based SACs, where the typical SACs are consisted of central metal atom, coordinated atoms and environmental atoms.

The activity and selectivity of the catalysts toward H₂O₂ production are mainly determined by the binding free energy of *OOH (G_{*OOH}).^[16] However, some works use *OH binding strength as a descriptor for the two-electron transfer ORR based on a scaling relationship of 3.2 ± 0.2 eV between the binding free energy of *OOH and *OH.^[22] Through the analysis of Density functional theory (DFT) simulations results as shown in Figure 2a, active sites with weak OOH adsorption such as Ni-, Cu-, Pt-, and Pd-N₄ should have better two-electron transfer ORR selectivity, while Mn- and Fe-N₄ locate at the left part of volcano plots exhibit high intrinsic four-electron transfer ORR activity. The difference comes from the inherent nature of the metal, such as the number of valence electrons, spin states and d-band centre positions, etc. Furthermore, for samples with the same central atom, the difference in coordination atoms will also cause a great change in the adsorption energy of key intermediates, but the recognition of regularity in this area has not been clearly reported. Moreover, for samples shared the same central and coordinate atoms (Co-N₄, Co-N₄(2H), Co-N₄(2O)) (Figure 2b), adjusting the atoms around the active centre can also affect the adsorption behaviour of OOH, for instance, the charge state of Co increases due to the influence of electron-rich species introduced on adjacent carbon and thus affects the performance of the two-electron transfer ORR.

Figure 2c describes a typical structure of a carbon-based SACs with a central metal atom, coordination atoms, environmental atoms, and framework atoms (mostly carbon atoms). As a metal atom that directly interacts with ORR feedstocks and intermediates, the central atom selection will have a significant impact on the reaction path; the coordination atoms are directly connected to the central metal atom through chemical bonds and share strong electronic interactions. Thus, the species of coordination atoms and coordination number will change the

chemical properties of the central atom and thus affect its intrinsic electrocatalytic properties. The environmental atoms defined in this paper are that not directly connected to the central metal atom, but the doping of hetero elements on the carbon skeleton will still realize the regulation of the central metal atom through long-range delocalization. Therefore, by rationally modulating the central metal atom, the coordinated atoms, and the environmental atoms, the intrinsic electrocatalytic two-electron ORR activity of carbon-based SACs can be efficiently boosted without sacrificing H_2O_2 selectivity. As an emerging application hotspot of SACs with promising potential, although some efforts fabricating various carbon-based SACs have been reported, principles of regulating the intrinsic electrocatalytic activity and selectivity of the carbon-based SACs towards H_2O_2 production are not sufficiently emphasized yet. An assorted summary of the current results and worth-exploring insights for further investigation are presented according to the above categories.

3.1 Central Metal Atoms

Figure 3. Central metal atom regulation. (a) Thermodynamic relations (volcano) lines for the two- (green solid line) and four-electron ORR (black solid line). The DFT calculated ORR onset potential values (circles) are on the left y-axis, while the experimental current densities (crosses and triangles), reported as $\ln(|j|)$, are on the right y-axis. Both are shown as function of the chosen reaction descriptor, and the DFT calculated OOH^* binding free

energy (G_{OH}), H_2O_2 selectivity (H_2O_2 %) and the number of electrons (n) at $+0.1 V_{\text{RHE}}$ are derived from RRDE data. Reproduced with permission.^[36] Copyright 2019, American Chemical Society. (b) Chemical structure of Co-TPP. (c) The corresponding H_2O_2 Faradaic efficiencies for each catalyst as a function of the applied potential. Reproduced with permission.^[64] Copyright 2020, Wiley-VCH (d) Binding energy of $^*\text{OOH}$, $^*\text{O}$, and $^*\text{OH}$ on M-SAC ($M = \text{Mn, Fe, Co, Ni, and Cu}$) and d-bond centre (open circle) of M atom in M-SAC ($M = \text{Mn, Fe, Co, Ni, and Cu}$) (e) Operando EXAFS spectra of Co-NC collected during H_2O_2 synthesis process; “OCP” stands for open-circuit potential. Reproduced with permission.^[65] Copyright 2020, Elsevier. (f) Linear relationship between the thermodynamic propensity for O–O bond preservation ($\Delta G_{\text{O}} - \Delta G_{\text{OOH}}$) and the H_2O_2 yields of model systems for atomically dispersed catalysts. Reproduced with permission.^[66] Copyright 2020, American Chemical Society.

The central metal atom has always been considered as the actual active site of metal-doped carbon electrocatalysts for ORR,^[67,68] therefore central metal atom selection will directly affect the intrinsic reaction path and activity of SACs. It is generally believed that the d-orbital electrons of the central atom directly interact with the p-orbital electrons of oxygen molecules and intermediates to complete the adsorption and electron transfer process,^[69] which makes the chemical nature of the central metal atom significantly important.

Instructive results were reported firstly by Strasser's group,^[36] in which 3d metals within a series of M-N₄ structures were investigated. To minimise the possible influence of other factors, such as geometry, etc., all samples were prepared from ZIF-8 using 1,10-phenanthroline and metal acetate as carbon and nitrogen sources and metal sources, respectively. The H_2O_2 selectivity of ORR at $0.1 V_{\text{RHE}}$ followed the order of Fe-NC(28%)<Cu-NC (36%)<Mn-NC(43%)<NC(45%)<Ni-NC(52%)<Co-NC(80%), and the opposite trend for the number of electrons transferred was observed (Figure 3a), indicating the favourable $2e^-$ transfer ORR pathway for H_2O_2 production over the Co-N-C catalyst. The practical H_2O_2 production capabilities of the Co-N-C catalyst under bulk electrolysis conditions were examined in an H-cell as well, in which the highest H_2O_2 production rate of $193.1 \text{ mmol g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$ was obtained in 0.1 M KOH at $0.1 V_{\text{RHE}}$. Due to the strong adsorption of OOH, Fe- and Mn-NC catalysts showed predominance of the four-electron pathway, while Cu- and Ni-NC showed an inactive performance due to the limitations in adsorbing intermediate. Co-NC catalyst was calculated

and experimentally proved as the closest to the top of the two-electron transfer ORR volcano (Figure 3a), maintaining catalytic activity while promoting selectivity towards H_2O_2 selectivity.

Although the coordination structure of Co-NC has been characterized in detail by extended X-ray absorption fine structure (EXAFS) technology, a Co coordination molecule with an accurately defined structure would be a more powerful example. Chang's group^[64] presented a supramolecular cobalt porphyrin for direct electrosynthesis of H_2O_2 . Unlike the general method of preparing SACs by pyrolysis, cobalt tetraphenylporphyrin (Co-TPP) (Figure 3b) was used as a building block to assemble the permanently porous supramolecular cage Co-PB-1(6) bearing six Co-TPP subunits connected through twenty-four imine bonds. The reduction of these imine linkers to amines yielded the more flexible cage Co-rPB-1(6). Both Co-PB-1(6) and Co-rPB-1(6) cages produced 90-100% H_2O_2 in neutral pH water (Figure 3c). The supramolecular SAC with a defined coordination structure (Co-N₄) eliminates the uncertainty of material characterization in traditional preparation strategies and provides evidence for discussing the intrinsic catalytic performance of Co-N₄. This work not only provides an alternative strategy for the conventional synthesis, but also a more accurate evidence for Co-N₄ as an effective catalyst for two-electron ORR.

Liu's group^[65] revealed the fundamental reasons more clearly by a proportional graph in which the binding energies of *OOH, *O, and *OH were generally scaled with the number of valence electrons in common transition metals from Mn to Cu in M-N₄ structure (Figure 3d). The higher amount of valence electrons in the central metal atom, the weaker the binding of these intermediates to the metal centre, which can be attributed to the fact that the d-band centre of M atom being shifted down in energy relative to the Fermi level from Mn to Cu.^[65] In detail, the interaction between d-orbitals of metal atom and 2p-orbitals of bonded O atom of intermediates shifts downward in energy, leading to a more filling state of anti-bonding states,

which weakens the M-O bonding from Mn to Cu. As discussed before, the higher binding energy between metal centres and OOH makes better ORR selectivity towards H₂O₂, which presents Cu and Ni as central metal atoms with higher selectivity compared with Mn. However, the high overpotential caused by the large *OOH reduction barrier and high O₂ activation energy is not satisfying when taking the activity into account. Significantly, the Co-N₄ SAC with optimal d-band centre shows $\Delta G^{*OOH} = 3.54$ eV at $U = 0.7$ V_{RHE} for the 2e⁻ transfer pathway, neither too strong nor too weak, being positioned nearly at the peak of the activity-volcano map, suggesting that the Co-N₄ SAC would be highly active for the 2e⁻ transfer pathway. In addition, the high barrier for *OOH reduction to *O intermediate on the Co-N₄ SAC compared with those on the Mn and Fe SACs would enhance the H₂O₂ selectivity of the Co-N₄ SAC. Subsequently, these five different transition metal SACs anchored on nitrogen-doped carbon (NC) (Mn-NC, Fe-NC, Co-NC, Ni-NC, and Cu-NC) were synthesized via pyrolysis of melamine, L-alanine, and the corresponding metal acetate mixture, and the experimentally obtained performance data were basically consistent with the theoretical prediction. At the same time, the operando extended X-ray absorption fine structure (EXAFS) spectrum helped to reveal the actual reaction active site and the rate-limiting step (Figure 3e). After switching N₂ to O₂ in the electrolyte, a dramatic enhancement of Fourier transformed intensity and a slight increase of Co-N distance to 1.35 Å from 1.25 Å were observed, indicating the adsorption of O₂ onto Co atoms, which pulled the Co atoms out of plane. At the potential of 0.6 V_{RHE}, part of the adsorbed O₂ was transformed to H₂O₂ via ORR, and the Co-N distance decreased to 1.32 Å. At higher cathodic potentials, the conversion of adsorbed O₂ to H₂O₂ via ORR became more rapid, and the surface coverage of O₂ became much lower because of the limited rate of O₂ adsorption, which explained the further decrease of the Co-N distance to 1.29 Å at 0.3 V versus RHE. This trend matches very well with the kinetic analysis above, in which Equation 11 is

the rate-limiting process at higher potential whereas Equation 8 becomes rate-limiting at lower potential.

For the prediction of the H_2O_2 selectivity of SACs, Kim^[66] presented a reasonable strategy. They reported a general synthetic strategy towards atomically dispersed precious metal catalysts, which consists of “trapping” precious metal precursors on a heteroatom-doped carbonaceous layer coated on a carbon support and “immobilizing” them with a SiO_2 layer during thermal activation. Among the SACs studied, the H_2O_2 selectivity was changed by the types of metals. The results showed that the Pt SAC exhibited the highest selectivity, and the Rh SAC possessed the best activity. As illustrated above, the preserve of the O-O bond can maximize the selectivity of H_2O_2 , however, there is still no report on quantifying the propensity for O-O bond cleavage. This trend is quantified in the article as the result of two competitive reactions (Equation 9 and 11). Consequently, the relative stabilities of $^*\text{OOH}$ and $^*\text{O}$ provide the thermodynamic driving force for O-O bond cleavage. The calculation results revealed that the difference between the O and OOH binding energies, $\Delta G^*_{\text{O}} - \Delta G^*_{\text{OOH}}$, which described the thermodynamic propensity for O-O bond preservation, and had a linear relationship with the experimental H_2O_2 yields of as prepared SACs (Figure 3f). Besides, a scaling relationship between $\Delta G^*_{\text{O}} - \Delta G^*_{\text{OOH}}$ and ΔG^*_{O} was observed. Therefore, the H_2O_2 selectivity can be predicted by O_2 temperature-programmed desorption (TPD, catalyst that has adsorbed O_2 was heated at a rate of $10^\circ\text{C}/\text{min}$, and the O_2 desorption temperature was detected. Stronger binding strength between O_2 and catalyst usually takes a higher temperature to desorb, vice versa. Therefore, the binding strength of O_2 can be described by the desorption temperature.) experiments in which the peak temperatures for O_2 desorption from the catalyst correlated to the oxygen binding strength. Experimental results further confirmed the relationship derived from the DFT calculations. This method provides a new strategy for screening SACs and selecting the central metal atom simpler from a direct experimental perspective.

To summarize the above analysis, carbon-based SACs including Co-N₄, have the most promising potential to be the next-generation catalysts that can realize the decentralized production of H₂O₂ from the two-electron transfer ORR. Nonetheless, the screen method of directly changing the central atomic element to get close to the apex of the H₂O₂ conversion volcano curve is too rough, in other words, some better active sites may be skipped.

3.2. Coordinated Atoms

For the SACs, the atoms that directly connect to the central metal atom are defined as coordinated atoms. From the view of coordination chemistry, the active site can be considered as a chelate where the central metal atom is coordinated with coordinated atoms via d-p σ -bonds and possibly back donating π -bonds. Therefore, regulating the coordinated atoms regarding their category and number, including multi-element coordination, will efficiently reconstruct the electronic structure of the active sites, thus affecting the adsorption behaviour of OOH on metal centres. Furthermore, for the same central metal atom, its coordination environment regulation can realize the fine adjustment of its position on the volcano curve, and then better balance its activity and selectivity.

Figure 4. Coordinated Atoms regulation. (a) Corresponding k^2 -weighted Fourier transforms of the Ni K-edge EXAFS spectra. (b) Scheme of the as prepared local structure. (c) H₂O₂ selectivity as a function of the applied potential. Reproduced with permission.^[70] Copyright 2020, Wiley-VCH. (d) Scheme of single Pd-sites supported on carbon material. Reproduced with permission.^[71] Copyright 2020, American Chemical Society.

The SACs combine the advantages of the "isolated site" of homogeneous catalyst and the heterogeneous structure of heterogeneous catalyst, which makes it stable and easy to separate from products.^[72] Inspired by metal-Schiff base heterogeneous catalysts, which can selectively reduce O₂ to H₂O₂,^[73,74] Zhang's group^[70] successfully synthesized carbon-supported Ni SACs with Ni-N₂O₂ sites using a simple "Schiff base ligand-mediated" pyrolysis strategy, in which Schiff base ligand (R,R)-(-)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine (Jacobsen's ligand) was used as the precursor. The author conducted K-edge EXAFS spectra (Figure 4a) to prove that the local coordination structure of Jacobsen-Ni, that is, Ni-N₂O₂ (Figure 4b) was still retained during the pyrolysis process. As shown in Figure 4a, the Ni-N₂O₂ catalyst showed a similar structure to the Jacobsen-Ni complex in terms of the nickel coordination, which was characterized by a peak at 1.42 Å, identical to a Ni-N₂O₂ local environment in Jacobsen-Ni complex.^[53] This bond length was much shorter than that Ni-Ni distance of 2.20 Å for metallic Ni foil and the Ni-Ni distance of 2.60 Å in NiO, and smaller

than the Ni-O distance in NiO (1.65 Å). The Ni-N₄ catalyst had a Ni-N distance of 1.40 Å, slightly smaller than the feature observed for Ni-N₂O₂. The introduction of two oxygen atoms to the same side Ni-N₄ species (Figure 4b) should be responsible for these subtle differences. However, such a slight change in the local structure caused a great change in the performances of electrocatalyst, making the central metal atom Ni that was originally used for electrochemical reduction of carbon dioxide^[54,75–77] and oxygen evolution reaction (OER)^[53] reached a maximum of ~96% selectivity of H₂O₂ at potentials between 0.4 and 0.5 V in the two-electron ORR (Figure 4c).

The practice of replacing all nitrogen with oxygen as coordinating atoms has also been successfully realized by Bian, Wang and co-workers^[78] who achieved this conjecture by a simple and surfactant-free reduction of Ni precursor on graphene oxidized (GO). EXAFS spectrum confirmed that the Ni atoms were dispersed in Ni-SACs owing to the dominant Ni-O peak at 1.63 Å and there were no peaks observed at 2.18 and 2.61 Å belonging to the Ni-Ni and Ni-O-Ni contributions, respectively. DFT modelling and calculation were also used to reveal the best coordination structure, in which four-oxygen-coordinated nickel single-atom centre was inclined to support selective HO₂[−] generation with a thermodynamic overpotential of ~0.1 V, which is particularly close to the ideal binding energy. The Ni-nanoparticle sample which was synthesized as a control group exhibited a relatively poor H₂O₂ yield (below 30%), whereas the H₂O₂% of the Ni-SAC catalyst was over 94% within the scope of 0.1-0.5 V_{RHE}. It is worth mentioning that the oxygen functional group in GO also contributed to the performance improvement.^[26,73] Excellent performance of full oxygen coordination Ni-SACs was also confirmed by Wang et al.^[79]

Freakley and co-workers^[71] successfully prepared single-atom Pd catalysts with Cl coordination to produce H₂O₂ through two-electron ORR and directly from molecular H₂ and O₂. The existence of Cl was recognized as C-Cl bonds and Pd-Cl bonds by XPS and low-energy

XAS. At the same time, the coordination number (3.99 ± 0.4) and bond length characteristics of Pd pointed out the four-coordinate structure of Pd and Cl. The excellent two-electron ORR selectivity was confirmed by current-voltage polarization curves ($>90\%$), and its mass-normalized activity reached to $72.8 \text{ A g}_{\text{Pd}}^{-1}$, which was higher than Pd nanoparticles. Additionally, chemical stability has also passed the after-used characterizations. The strong coordination ability of Cl ensured the isolation of Pd sites, and preferred the end-on oxygen adsorption mechanism, which in turn has better two-electron selective performance compared to Pd nanoparticles.

Figure 5. (a) Fourier transforms of k^3 -weighted Pt L_{III}-edge EXAFS, confirming that Pt species in Pt/HSC exhibit only Pt–S coordination (CN=3.8) without significant Pt–Pt coordination. (b) Proposed atomic structure of the Pt/HSC based on the buckyball-like structure of zeolite-templated carbon with possible thiophene- and thiolate-like functional groups at graphene edge sites, as well as coordinated Pt species (C: grey, H: white, S: yellow and Pt: purple). (c) Proposed ORR mechanism on the atomically dispersed Pt catalyst. Reproduced with permission.^[62] Copyright 2016, Nature Publishing Group. (d) Structural illustration of single Mo atom supported by O, S doped graphene substrate: Free energy diagram of 2e[−] ORR on three investigated substrates at equilibrium potential of the reaction, and atomic configuration of OOH* adsorption. (e) Calculated electron transfer number (n) and H₂O₂ selectivity (H₂O₂ %) as a function of the applied potential. Reproduced with permission.^[80] Copyright 2020, Wiley-VCH.

With smaller electronegativity and more complex electronic structure than oxygen, sulfur is also often doped into the carbon framework.^[31,81] Choi^[62] reported that a sulfur-doped zeolite-templated carbon could stabilize a relatively high loading of platinum (5wt%) as highly dispersed species including isolated atom sites and large sulfur content (17wt%), as well as a

unique carbon structure (that is, highly curved three-dimensional networks of graphene nanoribbons). The analysis based on Fourier transforms of k^3 -weighted Pt L_{III}-edge EXAFS (Figure 5a) and XPS-S_{2p} spectra revealed that Pt species in the as-prepared samples exhibited only Pt-S coordination (coordination number=3.8) without significant Pt–Pt bonding. Proposed atomistic structure (Figure 5b) of the Pt-S SACs based on the bucky bowl-like structure of zeolite-templated carbon^[82] with possible thiophene-and thiolate-like functional groups at graphene edge sites, as well as coordinated Pt species were inferred. An interesting kinetic point of view on the path of ORR was proposed, as shown in Figure 5c. When Pt-S SACs was solvated with water, it was found that the Pt centre can favourably interact with two water molecules, while losing its interactions with two sulfur atoms of thiophene moieties (0.63 eV downhill; Figure 5c-2). This is attributed to the stronger Lewis basicity of the oxygen lone pairs compared with that of the sulfur lone pairs in thiophene, which can activate Pt centre by a distortion of Pt centre and make it located out of the original square planar geometry.^[83] DFT energetics suggested that the first PCET (Figure 5c-3) step^[84] was the potential-determining in both the two-and four-electron pathways, where the calculated ORR limiting potential is 0.64 V_{RHE}. This implied that all elementary steps of the four-electron pathway become thermodynamically favourable under the bias potential of $U \leq 0.64$ V_{RHE}. Moreover, the competing step of the second PCET reaction towards the four-electron pathway (Figure 5c-5) was even more thermodynamically favourable than that towards the two-electron pathway (Figure 5c-4). The results indicated that electrocatalysis on atomically dispersed Pt catalyst was not controlled by thermodynamics, but rather by kinetics. Marcus theory^[85] was utilized here by taking the number of transferred proton–electron pair as a reaction coordinate for PCET. As shown in Figure 5c-8, in consideration of potential range $U < 0.8$ V_{RHE}, it was found that the two-electron pathway was always kinetically more favoured than the four-electron pathway. For the four-electron process, its second PCET process was accompanied by breaking the O-O

bond, which meant that larger reorganization energies were needed (1.84 eV for four-electron pathway vs. 0.55 eV for two-electron pathway). This was the dominant reason for more than 96% H₂O₂ selectivity.

Recently, a newly developed Mo SAC with a unique O, S coordination and a high metal loading over 10 wt% was synthesized for two-electron ORR with over 95% H₂O₂ selectivity (Figure 5e) by Qiao and his co-workers.^[80] Different from traditional M-NC samples, carbon atom in a hexagon ring adjacent to the sulfur dopant was considered to be the active centre, while Mo was the electron donor. Specifically, the Mo atom lost 0.86 electrons with adsorbed OOH (compared to the standalone Mo atom), suggesting the crucial contribution of Mo to the OOH binding ability in the Mo-O₃S-C structure (lower left scheme in Figure 5). When more sulfur was introduced into the coordination environment for Mo, such as Mo-S₄-C structure (lower right scheme in Figure 5d), the 2e⁻ ORR process was further facilitated (upper chart in Figure 4d) by the enhanced reaction intermediate adsorption strength (0.14 eV for OOH). Therefore, this work unravelled the critical role of the local coordination structure in SACs, which can significantly alter the electronic structure and adsorption behaviour on active sites, leading to promising tunability in reaction activity and selectivity.

Based on the above research, we can find that the selectivity of SACs can be significantly improved without sacrificing activity when oxygen group elements are doped as coordination atoms, so the central atom that does not apply for two-electron ORR originally can also be optimized. One possible explanation is that compared with N, O has a larger electronegativity (EN=3.44 for O and 3.04 for N) that matches the central metal atom well. For Ni as the central atom, it requires a larger electronegative atom to coordinate with thus to reduce its valence state and enhance the adsorption energy of *OOH, thereby addressing the insufficient-activity problem. While for Mo, the opposite situation can be solved by the coordination of the S atom

with weaker electronegativity (EN=2.58). Design strategies following this guidance shall be considered for the synthesis of SACs with high H_2O_2 catalysing efficiency.

3.3 Environmental Atoms

For the SACs, environmental atoms are those doped atoms that are not directly bonded to the central metal atom, usually doped on a carbon matrix or bonded to the coordination atoms. Considering the planar structure of the M-NC sites and the carbon-based substrates, omnipresent long-range delocalization of the d/p electrons exist within the M-NC SACs, which makes it possible for the atoms isolated from each other to have obvious interactions. Consequently, environmental atoms will influence the electronic structure of the central metal atom through the long-range delocalization effect although not directly bonded to it.

Figure 6. Environmental atoms regulation. (a) Schematic of the synergistic strategy of atomic $\text{Co-N}_x\text{-C}$ sites and oxygen functional groups for H_2O_2 electrocatalysis on noble-metal-free electrocatalysts. (b) Performance comparison in regard to reactivity and selectivity for H_2O_2 electrocatalysis on Co-POC-O , Co-POC-R , and POC-O electrocatalysts. The inset in (b) shows the mechanism scheme for synergistic H_2O_2 electrocatalysis. The carbon, nitrogen, oxygen, and cobalt atoms are marked with black, blue, yellow, and red, respectively. (c) High-resolution carbon 1s XPS spectra of Co-POC-O . Reproduced with permission.^[86] Copyright 2019, Wiley-VCH. (d) Calculated catalytic activity volcanoes for the production of H_2O (blue) and H_2O_2 (red), Cartoons of the complexes are given in the top panel (pink, Co; red, O; blue, N; grey, C; white, H). (e) Calculated OOH^* adsorption energies and relative charge states of the cobalt metal centre in $\text{Co-N}_4/\text{graphene}$ with 4H^* , 2H^* , O^* or 2O^* adsorbed near the cobalt atom. (f) Co 2p XPS spectra of $\text{Co}_1\text{-NG(O)}$ and $\text{Co}_1\text{-NG(R)}$. (g) Comparison of ORR performance at 1,600 r.p.m. (solid lines) and the simultaneous H_2O_2 detection current densities at the ring electrode (dashed lines) for NG(O) , $\text{Co}_1\text{-NG(O)}$ and $\text{Co}_1\text{-NG(R)}$ catalysts in 0.1 M KOH. Reproduced with permission.^[63] Copyright 2020, Nature Publishing Group. (h) Side and top view of CNT planes, where single Fe atoms may have direct coordination with both C and O. The vacant space is mainly due to the low detection

efficiency of atoms. Atom labels, Au in yellow, Fe in green, C in grey, and O in red, scale bars, 2 nm in (h). Reproduced with permission.^[20] Copyright 2019, Nature Publishing Group.

Like the selection of coordination atoms, the oxygen group, especially the oxygen itself, is also preferred to be using as the environmental atom. Modification of oxygen functional groups on nanocarbon prominently promotes the selectivity for the two-electron transfer ORR pathway to generate H_2O_2 . However, oxygen functional groups exhibit limited capability with high overpotential to produce H_2O_2 via ORR, and consequently, the assistance of additional active sites with high ORR reactivity is required. Atomic Co-NC sites have been proven to be effective catalysts in many cases to reduce oxygen in aqueous electrolyte.^[87,88] Nevertheless, such motif lacks the selectivity for H_2O_2 that oxygen feedstocks are usually reduced to water through the four-electron pathway instead of desired H_2O_2 .^[89] Whereas in a strategy proposed by Zhang et al.,^[86] the shortcomings are circumvented of the above two and the advantages of the high selectivity of oxidized carbon materials and the high activity of Co-NC materials are well combined (Figure 6a). The co-modification of atomic Co-NC sites and oxygen functional groups was performed by pyrolysis of the predesigned precursor and following oxidative acid treatment. The best performance was achieved by Co-POC-O (Figure 6b), in which the XPS spectrum confirmed the existence of oxygen as a carbon-oxygen single bond (C-O, 59.3 at%) and a carbon-oxygen double bond (C=O, 40.7 at%)(Figure 6c). Although the authors have not precisely confirmed the exact doping position of O, whether it was directly bonded to the Co-NC group to form Co-NC-O or Co-NC=O moiety or not, the fact that the doping of O in carbon substrate can indeed improve the activity and selectivity of Co-NC towards H_2O_2 electrosynthesis at the same time was well verified.

A clearer example of oxygen doping was subsequently provided by Hyeon and his collaborators.^[63] Periodic DFT calculations were performed on various M-N₄/graphene catalysts, where worth to mention that a correction to account for the water-induced stabilization was included. Figure 6d showed the volcano plot for ORR activity as a function

of the *OOH adsorption energy, similar to other works, H₂O₂ production was energetically preferred to H₂O production for Ni and Ag. However, considering their high overpotentials, slightly modify of highly-active Co-N₄/graphene was more appealing regarding the by-product (H₂O) of this process. An evidence chain was successfully constructed: "doping of electron-rich groups (O) on carbon near the Co-N₄ moiety" → "charge state of Co becoming more positive (Figure 6e)" → "increasing the adsorption energy of *OOH (Figure 6d)" → "improving the selectivity of H₂O₂". Subsequently, the Co-N₄ sites were anchored on graphene oxide by the mild reduction strategy while retaining many C-O-C moieties to form Co₁-NG(O). Compared with the fully reduced sample (Co₁-NG(R)), the upshift of Co 2p XPS spectra (Figure 6f) was observed and the spin-orbit splitting value ($\Delta\text{Co}=15.875$ eV) of Co₁-NG(O) was larger than that of Co₁-NG(R) ($\Delta\text{Co}=15.504$ eV), which indicated that Co₁-NG(O) catalyst possessed partially oxidized Co single atoms. In addition, Co₁-NG(O) exhibited a significantly higher activity (Figure 6g) for H₂O₂ production than NG(O), which was commonly seen in carbonaceous catalysts,^[26,90] and an enhanced selectivity compared with electron-rich Co metal centres (Co₁-NG(R)).

For the practical application scenario of H₂O₂ produced by the electrochemical method and used for bacteria elimination, Wang's group^[20] showed a great example, which also illustrated the effect of environmental atoms on catalytic performance. In order to initiate the Fenton reaction, Fe was used as the central atom. However, in view of the excellent four-electron ORR performance of Fe-N₄-C, the authors constructed Fe-C-O (Figure 6h) on carbon nanotubes through the strategy of freeze-drying and thermal annealing. The experimental results and DFT calculations both showed that when O was used as the environmental atoms, the selectivity of H₂O₂ was significantly improved compared to Fe-C-N.

The above works manifest that the introduction of suitable hetero-environmental atoms enhances the performance of SACs in H₂O₂ production. However, current research mainly

focuses on oxygen doping, considering that oxidized carbon^[26,65,91,92] itself is a well-known catalyst, the further doping of oxygen causes ambiguity in identifying the catalytically active sites. In addition, the fine characterization of the heteroatom doping^[81,93–95] structure also needs to be developed^[96] to further prove the structure-performance relationship more clearly.

4. Summary and outlook

Figure 7. (a) Summary of the H₂O₂ selectivity of the reported catalysts as a function of the applied potential. Data from: PtHg₄, Ref^[16], Copyright 2013, Nature Publishing Group; Pt/HSC, Ref^[62], Copyright 2016, Nature Publishing Group; Mn-NC, Fe-NC, Cu-NC, Co-NC and Ni-NC Ref^[65], Copyright 2020, Elsevier; Co₁-NG(O) and Co₁-NG(R), Ref^[63], Copyright 2020, Nature Publishing Group; Co-POC-O, Ref^[86], Copyright 2019, Wiley-VCH; Fe-CNT and Red. Fe-CNT, Ref^[20], Copyright 2019, Nature Publishing Group; Mo₁/OSG-H, Ref^[80], Copyright 2020, Wiley-VCH; Ni-N₂O₂, Ref^[70], Copyright 2020, Wiley-VCH; Ni-SA/G-O, Ref^[78], Copyright 2020, American Chemical Society; Pt/CNT_IL_SiO₂ and Rh/CNT_IL_SiO₂, Ref^[66], Copyright 2020, American Chemical Society. (b) Computed U_L values of 31 SACs in comparison with the PtHg₄ benchmark (U_L = 0.46 V). Reproduced with permission.^[97] Copyright 2019, American Chemical Society. (c) Proposed directions towards advanced SACs for two-electron transfer ORR.

SACs lead the wave of single-atomization of traditional catalysts with maximum atom-utilization and well-defined as well as diversely adjustable structure. The study of their intrinsic properties is essential to develop their catalytic performance and expand their broader application scenarios. For the synthesis of H₂O₂ via ORR on SACs, the electronic structure of active sites is believed to determine the adsorption behaviour of the only intermediate, OOH; the latter can be chemically modulated at three levels concerning the central metal atom, the coordination atoms, and the environmental atoms, respectively.

We have systematically summarised the available reports on promising single-atom catalysts for the production of H₂O₂ via the two-electron transfer ORR (Figure 7a); in particular, using

Ni, Fe, Co, Mo, and other low-cost metals as the active single-atom centre exhibits enormous potential. Moreover, the coordination-structure adjustment and environmental-atoms regulation based on these central metals may become future research hotspots. Furthermore, for the coordination of the central atom, introduction of oxygen group elements has proven to improve H_2O_2 selectivity. The influence of the electronegativity of environmental atoms on the central atom and its regulation patterns have been fully discussed. Although remarkable achievements have been made, there are still many issues remain controversial and need to be addressed in the future research, where both opportunities and challenges coexist, as highlighting below.

(1) Diversely structural design

For the selection of the central atom, high-throughput theoretical calculations can provide us with some useful guidance. Huang and his co-workers^[97] screened 210 SACs from the combination of 30 metal atoms and 7 framework structures (Figure 7b) via DFT computations and machine learning, in which Zn-Pc-N₄ and Zn-Py-N₄ stood out after rounds layers selection. This result and the screening process itself provide new candidates and ideas for the selecting the central atom, although present experimental studies cannot meet the prediction from DFT computations. At the same time, the current attempts to use precious metals and rare earth metals as central atom are too conservative, despite the reserve issues, the excellent stability should be highlighted which is unmatched by transition metals in the fifth period, considering the offensive nature of H_2O_2 .

An important feature of carbon-based materials is that a variety of heteroatoms doping can be achieved, which is embodied in two aspects. Firstly, more diverse coordination structures can be realized (Figure 7c). Although the four-coordination structure has been extensively studied, the five-coordination structure, which could be more stable than the three-coordination structure and more active than the six-coordination structure, is rarely reported. Besides, the

introduction of other elements with suitable coordination ability, multi-elements co-ordination and guest group,^[98–101] will achieve finer regulation of the electronic structure. Secondly, more diversely environmental atoms doping will also influence catalytic performance. Current researches mainly focus on the doping of oxygen elements, in fact, the doping of boron,^[93] sulfur,^[31,102] fluorine,^[103] etc. are considered to affect the selectivity of the two-electron transfer ORR on carbon materials. And it is obvious that these affections can also be synchronized to central metal atom and thus change the adsorption behaviour through electronic conjugation. Although it may be exhausting to realize these diversified designs through experiments, high throughput screening based on machine learning and DFT calculation may narrow the scope down and provide us with a more in-depth understanding of the regularity of the structure-performance relationship at the periodic table level. Moreover, the realization of these designs requires the support of advancements in synthesis and characterization techniques.

(2) New synthesis strategies

The accomplished design of the complex structures requires new synthesis strategies (Figure 7c). On one hand, accurately controlled synthesis at the atomic level remains a significant challenge in the field of catalytic materials, as for SACs used in electrochemistry, the contradiction between widely utilized pyrolysis process for carbon-based SACs fabrication to achieve better conductivity and the collapse of the pre-designed precursor structure still needs more ingenious strategies to conquer. Therefore, non-pyrolysis synthesis pathways with high time-efficiency are highly considered to construct the well-defined active sites. On the other hand, the aforementioned complex-structure design requires more advanced precursor synthesis strategies. Perhaps some inspiration can be obtained from biological macromolecules or metal coordination catalysts originally used for organo-catalysis. These diversified

molecules as precursors can provide more diversified and well-defined coordination structures, making the subsequent synthesis process clearer.

(3) Advanced characterization technique

As an important part in the structure-performance relationship evidence chain, detailed characterization results are necessary factors for the success of the synthesis strategy (Figure 7c). Additionally, precise characterizations are of great importance to describe the single-atom structure accurately, especially under working conditions. High-resolution microscopy, X-ray absorption spectroscopy, X-ray photoelectron spectroscopy and other routine characterization methods can only obtain obscure environmental information around the central metal atom, which significantly restricts the design of complex active centres. Cryogenic electron microscopy, time-of-flight secondary ion mass spectrometry,^[104,105] Pair Distribution Function (PDF) analysis and other advanced characterizations at sub-nanometre scale are essential in local structure identification. In particular, the applications of these characterization techniques in the in-situ studies will greatly advance our understanding of the underpinning science.

(4) Application-oriented H₂O₂ production process

Considering the potential usage fields of the H₂O₂ product, several factors including H₂O₂ yield, the pH value of the reaction system and H₂O₂ storage issues should be taken into accounts. Compared to the FE selectivity, the H₂O₂ yield should be the criterion to evaluate catalyst. Thus, more efforts should be paid on improving the catalyst activity instead of pursuing the FE selectivity only. Considering the H₂O₂ suffers a severe decomposing in the alkaline solutions, the reaction system should also be beneficial to the storage of hydrogen peroxide. Based on these considerations, we recommend the pH-neutral and acidic solutions as the reaction electrolytes. Some novel mechanisms could be introduced for designing an eligible electrode which could meet all the requirements. For example, the arrayed electrode can achieve rapid mass transfer and increase the overall efficiency of the reaction;^[106] a superaerophilic surface

modification could enrich the oxygen reactant and boost the current density. In general, SACs design for H₂O₂ production device, based on the two-electron ORR, is of great potential, but at the same time, more comprehensive exploration is still needed.

To summarize, carbon-based SACs have proven ability to serve as a promising, alternative electrocatalyst for efficient H₂O₂ production via the two-electron transfer ORR pathway. In this review, the design strategies of the carbon-based SACs for the two-electron transfer ORR are discussed in detail through several examples; and strategies for regulating intermediate OOH adsorption energy, in order to achieve high H₂O₂ selectivity, are explained from three viewpoints, i.e., the central metal atom, the coordinated atoms and the environmental atoms. These new understandings of SACs could be extended and applied to many aspects of heterogeneous catalyst design. Considering the recent rapid progress in the SACs and continuous endeavours, wider application scenarios that can lead to a more sustainable world will be inspired by the ambitious yet rational design of emerging carbon-based SACs.

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